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(71) Sökande Sandvik AB, Sandviken SE  
Applicant (s)

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Görel Gustafsson  
Avgift  
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This metal disintegrating mechanism was already known since the 1940's as so-called "metal dusting". The metal dusting process is known to be inhibited by the presence of sulphur in the carbon containing gas. Increased environmental demands and the requirements of newly developed catalysts have made low-sulphur conditions necessary, which has led to an increase in metal dusting related failures.

As earlier mentioned, metal dusting is a form of catastrophic carburisation, where the metal disintegrates rapidly into coke and pure metal or other types of metal rich reaction products. Metal dusting is in the present case taken to mean the process whereby a metal or an alloy is attacked by a carbon rich gas and corroded into a mixture of coke/carbon and metal rich particles. Metal dusting typically occurs in gases that are initially supersaturated with respect to carbon, i.e. having a carbon activity greater than unity. The corrosion products of the metal dusting process are metal rich compounds and carbon rich compounds. The carbon rich compounds are typically in the form of coke, i.e. a solid carbonaceous deposit that can contain varying concentrations of e.g. hydrogen, nitrogen, oxygen etc. The metal rich compounds can be different depending on e.g. the oxygen content of the system and the alloy composition, as well as the operating temperature and pressure. Typical metal rich compounds are metal carbides, metallic alloys with dissolved carbon and oxides of the component metals in the alloy.

Metal dusting occurs most commonly when a carbon containing gas is cooled from a high temperature at which it is at or near equilibrium. Often this equilibrium state is reached with the help of catalysts, which means that at the initial equilibrium, the gas phase reaction rates are low. During cooling, the gas will not be able to equilibrate, due to sluggish kinetics, and as a consequence the gas becomes strongly carburising. In most applications where metal dusting is a problem, such as for example in steam reforming applications processes, the gas is cooled in order to retain the equilibrium achieved at high temperature over a catalyst. It is thus a necessary feature of such processes that metal dusting can occur, and it is not possible to design the process so as

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to avoid metal dusting, carburisation or coking entirely. According to P. Szakalos, "Mechanisms of metal dusting on stainless steel", Licenciate thesis, 2002, ISBN 91-7283-260-6 metal dusting is thus likely to occur in those components where the gas is cooled, such as waste heat boiler, steam superheaters and in heat exchange reformer units. The temperature range in which metal dusting is most likely to occur is 400-800°C.

The atomised metal particles produced by metal dusting can be transported with the process gas, accumulate downstream on various reactor parts, and throughout the whole reactor system, metastasise catalytic coking that can create blockage.

It is generally appreciated that metal dusting is a large concern in the production of hydrogen and syngas ( $H_2/CO$  mixtures). In these plants, methane and various other higher hydrocarbons are reformed or partially oxidised to produce hydrogen and carbon monoxide in various amounts for use in producing other higher molecular-weight organic compounds. Increased reaction and heat-recovery efficiencies of the processes necessitate operating process equipment at conditions that favour metal dusting.

The need for increased heat recovery in ammonia-synthesis processes has caused metal dusting problems in the heat-recovery section of the reformed-gas system as well as in the reformer itself.

Metal dusting is also a problem in direct iron-ore reduction plants wherein reformed methane is dried and reheated to enhance ore-reduction efficiencies. Metal dusting occurs in the reformer, reformed-gas reheat and piping upstream of the ore-reduction.

Metal dusting is also experienced in the heat-treating industry in equipment that handles items being treated (annealed, carburized).

Gases used in heat treating mix with oil residue on the items to form gases that are chemically favourable for metal dusting.

Gas mixtures used for carburizing can also cause metal dusting if control of chemistry of the process is not taken care of.

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optimum properties. However, even with a total content of Fe+Ni+Co+Mn of up to 6 weight-%, the alloy is superior to the standard material Alloy 800HT.

#### EXAMPLE 5

5 Fig. 6 shows a section of a phase diagram Cu-Ni-Al calculated with Thermo-calc for a given Al-content of 8 weight-%. Graph 1 shows the solidus/liquidus temperature, graph 2 shows the area of stability for the phase NiAl, graph 3 shows the area of stability for the cubic close-packed solid solution of copper and nickel, which also can contain minor contents of e.g. aluminium. Graph 4 shows the area of stability for the phase, which in the pure Cu-Al-system is called  $\beta$ .

10 Fig. 6 and Table 6 show the effect of different contents of copper, nickel and aluminium in an alloy of 92 weight-% (Cu+Ni) and 8 weight-% Al at the solidus- and liquidus temperatures. The Figure 6 shows that only by increasing the content of nickel above 20 weight-% its melting point can be brought to exceed 1100°C.

15 Fig. 7 and Table 6 show the effect of the Ni, Cu and Al contents on the solidus temperature and carbon solubility in an Cu-Al-Ni alloy. The diagram shows, that for nickel contents above approximately 10 weight-% the solubility of carbon is strongly increased with increasing nickel content. The rate of carburization of an alloy is to a high extent determined by the solubility of carbon in the alloy and also the phenomena of metal dusting and coking are expected to increase with increasing carbon solubility. Therefore, it is desirable that the solubility of carbon in the alloy is as low as possible, and a consequence of this is that the nickel content should be lower than 10 weight-% in order to obtain an optimum resistance to carburization, coking and metal dusting, preferably lower than 1 weight-%.

20 The reason for such low level of the Ni-content is required in order to obtain optimum properties is, that nickel, besides affecting the solubility of carbon also catalyzes coking, which is unfavorable.

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Table 6

Example	Ni weight-%	Al weight-%	Cu weight-%	Solidus temperature °C	Carbon solubility at 750°C g carbon/g alloy
R	0	4	96	1070	2,50E-13
S	2	4	92	1080	3,30E-13
T	5	4	91	1090	3,50E-13
U	10	4	86	1100	6,60E-13
V	20	4	76	1130	5,00E-12
W	0	8	92	1040	9,65E-13
X	2	8	90	1030	8,22E-13
Y	5	8	87	1040	5,40E-13
Z	10	8	82	1070	3,00E-13
AA	20	8	72	1100	8,00E-13
Comp. Example 1	60	4	36	1270	1,90E-07
Comp. Example 2	60	8	32	1200	7,00E-08
Comp. Example 3	30	4	66	1160	7,00E-11
Comp. Example 4	40	4	56	1190	1,20E-09
Comp. Example 5	50	4	46	1230	1,90E-08
Comp. Example 6	30	8	62	1130	7,00E-12
Comp. Example 7	40	8	52	1150	1,00E-10
Comp. Example 8	50	8	42	1180	2,40E-09

## EXAMPLE 6

5 The person skilled in the art realizes that for the product according to the present invention it is necessary to be designed with a load carrier at elevated temperatures, i.e. temperatures above approximately 400°C. With this purpose a Cu base alloy can be machined to a component in a composite or bimetallic composite solution, which will be used as construction material in the different shapes as mentioned above. The latter is especially valid if the alloy has low contents of iron and nickel.

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The product is in the shape of tubes or plate or strip or wire, where the inner load-carrying layer is coated at one or both surfaces with the Cu base alloy specified in previous examples. Some of the methods, which can be used in order to produce a composite solution of the alloy and a load carrier are co-

- 5 extrusion, co-welding or co-drawing and shrinkage of one tube on the load carrying component and one outer and/or inner tube of the alloy according to the invention, possibly followed by a heat treatment in order to obtain a metallurgical binding between the components. A similar method for the production of plate or strip is to hot- or cold-roll together two or more plates or
- 10 strips. Composite plates or -tubes can also be produced by explosion welding of two or more different plates or tubes of a load carrier and the alloy according to the invention. An outer- and/or inner-component can also be applied on a load carrier by help of a powder metallurgical technique, such as HIP (Hot Isostatic Pressing) or CIP (Cold Isostatic Pressing). In these cases the load
- 15 carrier could be in the shape of tubes, pipes, plate, strip or wire or other suitable product form. After pressing, the formed composite will be further machined by e.g. hot extrusion and/or welding, drawing and forging.

Other methods for the production for the production of composite material are

- 20 electrolytic coating of copper and aluminium on the load carrying component, possibly followed by an annealing in order to homogenize the coating or a gas phase deposition of copper and aluminium by e.g. vaporization, pack cementation, sputtering, chemical vapor deposition (CVD) or other methods. Aluminium and copper can also be deposited on the load carrier e.g. by dipping
- 25 in a melt or by overlay welding. These methods are possible to use in order to produce all of the above-mentioned product forms. Different coating methods can be used in order to supply copper and aluminium to the alloy. In such cases, a final heat-treatment is required in order to homogenize the alloy with the purpose to keep its corrosion properties.
- 30 Composite strip or composite plates, produced according to the above description can be welded together to longitudinal welded or helical welded composite tubes with the Cu base alloy on the inner and/or outside of the tube.

(UNS N08811) with a protective layer of a Cu-base alloy of composition Cu-8.5 weight-%Al-1.0 weight-%Si-0.5 weight-%Fe on both inner and outer surfaces. One example of such a tube has a diameter of 60.3 mm and a total thickness of 3.91 mm. In this finished product, the outer corrosion resistant layer has a

5 thickness of 1.0mm, and the inner corrosion resistant layer a thickness of 0.7mm, whereas the load bearing component has a thickness of 2.2 mm. At 900°C, this means, that the maximum allowable pressure drop according to the ASME boiler and pressure vessel code, section VIII, division I, is approximately 5.5 bar. Since the gas exchanges heat with itself, the pressure drop across the  
10 tube wall is expected to be less than 5 bar, even in processes that operate at absolute pressures in the range 10-100 bar. Thus, the product described in the previous section fulfills the necessary requirements to be used at as high temperatures as 900°C.

15 It should be clear to the person skilled in the art that the tubular product with the corrosion resistant alloy covering only the inner or only the outer surface are also possible with a wide range of dimensions and compositions of the Cu base alloy and the load bearing alloy.

20 EXAMPLE 8

An example of this is a tube which conducts a gas with a carbon activity greater than unity at a temperature range of 450-700°C in its interior and on its outer surface is cooled by air with temperature in the range 200-700°C. For this reason such a tube is covered with a metal dusting resistant Cu-base alloy on  
25 its inner surface, but the outer surface must still have a sufficient oxidation resistance with respect to the hot air. Using a proven alloy such as Alloy 600 (UNS N 06600) with 6 mm wall thickness and 2 mm thick Cu-7Al-0.2Si-0.5 weight-%Ni alloy on the inner surface allows at least 10 years service life with an internal pressure of 10 bar.

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**EXAMPLE 9**

A further example of is a tube which conducts steam in its interior and which is heated from the outside by a gas with a carbon activity greater than unity at a temperature range of 200-600°C. In this case, the outer surface is exposed to

- 5 the metal dusting conditions, whereas the inner surface is not exposed to any carbon related corrosion. For this reason such a tube is covered with a metal dusting resistant Cu-base alloy on its outer surface, and an alloy with sufficient steam corrosion resistance and mechanical strength is used as the load bearing member. One alloy that fulfils these demands is Alloy 800HT (UNS N 08811).
- 10 With a tube of outer diameter 50 mm and a wall thickness of 3.7 mm, using a 0.9mm thick Cu-5.8 weight-%Al-1.0 weight-%Si layer on the outer tube surface. In that case the Alloy 800HT thickness is 2.8 mm which means that the maximum internal steam pressure that can be allowed is 100 bar.

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## Claims

1. Use of a copper-base alloy containing (in weight-%):

Al 2 - 20

Si ≥0 - 6

5 One or more of the group of Rare Earth Metals (REM),  
such as yttrium, hafnium, zirconium, lanthanum and /or cerium  
up to 1.0 of each element  
in total up to 3.0

One or more of the elements iron, nickel, cobalt and maganese,  
10 in total up to 20

Cu balance

and normally occurring alloying additions and impurities.

In CO-containing atmospheres, and/or hydrocarbon containing atmospheres  
or solid carbon containing processes, such as gasification of solid  
15 carbonaceous materials, thermal decomposition of hydrocarbons and  
catalytic reforming, particularly, catalytic reforming under low-sulfur, and  
low-sulfur and low-water conditions.

20 2. Use of a copper-base alloy according to claim1 in CO-containing  
atmospheres, and/or hydrocarbon containing atmospheres or solid carbon  
containing processes, i.e. processes such as gasification of solid carbonaceous  
materials, thermal decomposition of hydrocarbons and catalytic reforming,  
particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water  
25 conditions at temperatures between 400 and 900°C and at pressures below 100  
bar.

3. Use of a copper-base alloy according to claims 1 and 2 as one  
component in a composite material in the shape of tubes, pipes, plate, strip and  
30 wire in CO-containing atmospheres, and/or hydrocarbon containing  
atmospheres or solid carbon containing processes, for example, gasification of  
solid carbonaceous materials, thermal decomposition of hydrocarbons and  
catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-  
sulfur and low-water conditions.

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4. Use of a copper-base alloy according to claim 1 to 3 as one component in a composite material.

5 5. Use of a copper-base alloy according to claim 1 to 4, where the copper-base alloy is provided in a minimum thickness of the corrosion resistant component of at least 0.5 mm for use at temperatures of 450-650°C in said composite form.

10 6. Use of a copper-base alloy according to claim 1 to 4, where the copper-base alloy is provided in a minimum thickness of the corrosion resistant component of at least 1.0 mm for use at temperatures above 650°C in said composite form.

15 7. Use of a copper-base alloy according to claim 1 to 6 as construction material in the shape of tubes, pipes, plate, strip and wire.

8. Copper-base alloy according to claims 1 to 7, characterized in that said alloy is resistant or immune to carburization, metal dusting and coking and resistant to oxidation and has the following composition (all contents in weight-%):

Al 2 - 20

Si ≥0 - 6

One or more of the group of Rare Earth Metals (REM),

such as yttrium, hafnium, zirconium, lanthanum and/or cerium

up to 1.0 weight-% of each element

in total up to 3.0

One or more of the elements iron, nickel, cobalt and manganese,

in total up to 20 weight-%

30 Cu balance

and normally occurring alloying additions and impurities.

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9. Copper-base alloy according to claim 8, characterized in that said alloy comprises up to 20 weight-% Al, preferably 4-13 weight-% Al, most preferably 4-9 weight-% Al and the balance Cu and normally occurring alloying additions and impurities.

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10. Copper-base alloy according to claim 8, characterized in that said alloy comprises up to 6 weight-% Si, preferably up to 5 weight-% Si and the balance Cu and normally occurring alloying additions and impurities.

10 11. Copper-base alloy according to claim 8, characterized in that said alloy comprises one or more of the group of Rare Earth Metal (REM), Yttrium, Hafnium, Zirconium, Lanthanum and/or Cerium in a content up to 1.0 weight-% each.

15 12. Copper-base alloy according to claim 8, characterized in that said alloy comprises one or more of the group of Rare Earth Metal (REM), Yttrium, Hafnium, Zirconium, Lanthanum and/or Cerium in a total content content up to 3.0 weight-%, preferably 0.5 weight-%, most preferably 0.01-0.2 weight-%.

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13. Copper-base alloy according to claims 7 to 12, characterized in that said alloy is resistant to oxidation in CO-containing atmospheres, and/or hydrocarbon containing atmospheres or solid carbon containing processes, for example, gasification of solid carbonaceous materials, thermal decomposition of hydrocarbons and catalytic reforming, particularly, catalytic reforming under low-sulfur, and low-sulfur and low-water conditions at temperatures between 400 and 900°C and at pressures below 100 bar.

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Figure 1

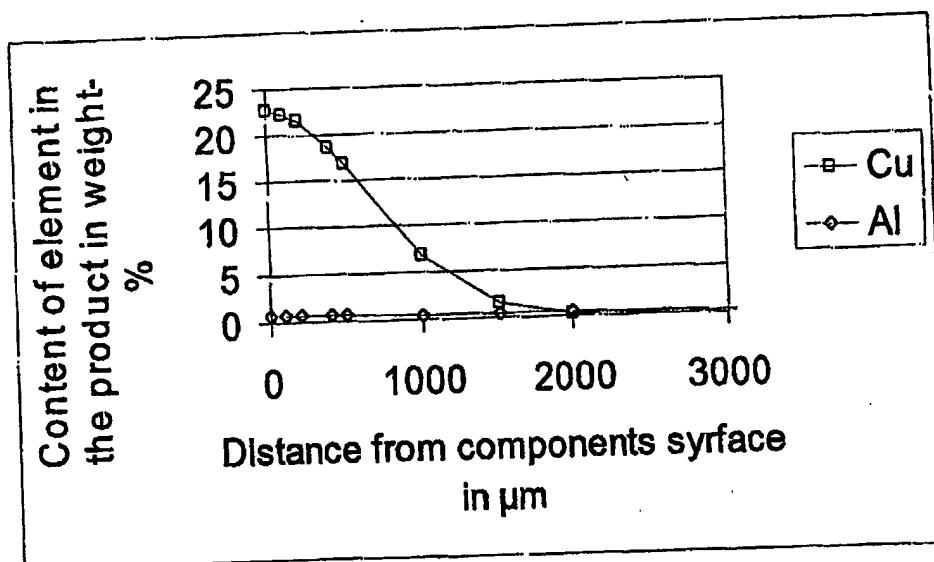


Figure 2

